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FACTORS IN SEWAGE CHLORINATION-II

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FACTORS IN SEWAGE CHLORINATION - II

by

C. E. Rhines and W. P. Cheevers
January 7, 1964

I. OBJECT:

This study has been directed at determining factors important in sewage chlorination. Developments are summarized for review.

II. SUMMARY:

1. Controlled bio-oxidation looms as a key to effective chlorination. Aeration with fecal organisms prior to chlorination has proved to be much more effective than initially indicated (1). Ten fall-season samples averaged a 70% demand-reduction during aeration. A sewage adequately conditioned to an optimum bio-oxidative state will maintain a stable chlorine-residual level for an extended period.

2. Additional observations have confirmed the generally marked increase in chlorine demand and interference with disinfection by amino acids. The absence of these effects with proteins indicates that trouble is due to free amino groups.

3. Efficiency of aeration is dependent on microbial activity. Observed changes during aeration are chlorine-demand reduction, flocculation of solids, deamination of amino acids, and synthesis of polypeptide-type nitrogen from amino acids. Cellular protein is formed and is separated with the flocculated fraction. Amino acids vary in their susceptibility to deamination.

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16. Abstracts

This study was directed at determining factors important in sewage chlorination. It was found that: (1) controlled bio-oxidation looms as a key to effective chlorination; (2) additional observations confirmed the generally marked increase in chlorine demand and interference with disinfection by amino acids; (3) efficiency of aeration is dependent on microbial activity; (4) cystine, cysteine, and uric acid have high-chlorine demands, but cause little or no interference with chlorine disinfection; (5) subchlorination disinfection was observed, but was regarded as a minor factor; (6) a dechlorinating activated sludge system was a means of drastically reducing the high toxicity of chlorinated sewage effluent to fish; and (7) low temperature markedly retards chlorine disinfection.

17. Key Words and Document Analysis. 17a. Descriptors

17b. Identifiers/Open-Ended Terms

*Sewage treatment
*Chlorination
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4. Cystine, cysteine, and uric acid have high chlorine-demands, but cause little or no interference with chlorine disinfection. Toxic chlorine products are indicated.

5. Subchlorination disinfection has been observed, but is regarded as a minor factor. Substantial chlorine residues are required for reliable disinfection.

6. A dechlorinating activated sludge system has been demonstrated as a means of drastically reducing the high toxicity of chlorinated sewage effluent to fish. The system reduces indicator organisms to a negligible level.

7. Low temperature markedly retards chlorine disinfection. Adequate treatment time will lead to effective chlorination. Chlorine toxicity has extraordinary persistence in cold sewage.

III. CURRENT ACTIVITIES:

1. Aeration Prior to Chlorination

Initial studies (1) on this project were designed to obtain some badly needed information on bactericidal action of chlorine in sewage. The sewage was pasteurized and alum flocculated to reduce the natural bacterial population and to remove suspended matter which interfered with the residual chlorine test. This low bacteria count sewage was subjected to aeration studies after inoculation with sewage organisms. Benefits, ranging from small to considerable, were noted. Follow-up studies were carried out on sewage aerated without pasteurization.

Ten fall-season samples, aerated 5 to 24 hours, underwent an average chlorine demand reduction of 70% during aeration (Table I). These samples were in the 20° to 28°C (range) - room temperature - during aeration.

The aerobic treatments applied to the samples in Table I utilized the large population of fecal bacteria normally found in sewage. Benefits undoubtedly arose through oxidizing strong reducing substances and preventing the formation of reducing agents by anaerobic action. In addition, aerobiosis favored the deamination of amino acids and the conversion of amino acids to protein and peptone. A bio-flocculation process occurred with a demand-bearing sediment separating readily after aeration.

Earlier work demonstrated that nitrite formation would interfere sericusly with chlorination. The data of Table I demonstrate that simple aeration of sewage does not encounter the high chlorine-demand introduced by nitrite-formers. This difficulty has been encountered only when a nitrifying inoculum was introduced.

Sewage treated by aeration followed by decantation from the flocculated sludge has been highly susceptible to chlorination. A residual value of 0.50 to 1.0 ppm is reached with a relatively light chlorine application. This residual chlorine level is much more stable than the residual level of untreated sewage. The initial high disinfection rate usually encountered immediately after chlorine introduction continues for a prolonged period, whereas, in unconditioned sewage, the disinfection rate starts dropping with residual chlorine drop immediately after completion of chlorine dosage.

It is now practical to reduce the E. coli count to negligibly low levels by extended exposure (one to many hours). It follows, from known correlations between the relative destruction of E. coli and pathogenic bateria, that the same low count can be achieved for the latter.

Figure 10 of the original report (1) illustrates how disinfection continues for a long period in an adequately chlorinated sewage. Disinfection rate can be much higher and reaction time much longer in a sewage given optimum bio-oxidative conditioning. It should be particularly noted that a sewage adequately conditioned to an optimum bio-oxidative state will maintain a high residual chlorine level over an extended period. The data of Figure 10 and subsequent studies indicate that initial sewage organisms equal to E. coli in susceptibility to chlorination can be reduced to 10^{-20} and less fractions of their starting count. This phenomenon can be regarded as a satisfactory approach to sterility.

In addition to the types of changes noted in section 3 following, aeration was observed to offset demand development from anaerobic decomposition products of carbohydrates. Anaerobic sewage supplemented with dextrose increased sharply in demand while the aerated counterpart decreased in demand.

2. Effect of Amino Acids

It was stated in the original report (1) that a large number of amino acids sharply increased the chlorine demand of sewage and markedly interfered with chlorine disinfection. Since, it

has been observed that the proteins, gelatin and egg albumin, have a negligible effect on the chlorine demand under the same test conditions. Gelatin exhibited no interference with chlorine disinfection in a bacteriological check. These combined observations form evidence indicating that free amino acid groups are largely responsible for the interfering action of proteinaceous substances.

3. Effect of Aeration with Sewage Bacteria on Amino Acid Supplements and on Flocculation

A number of experiments have been carried out involving the effect of aeration in the presence of sewage bacteria on amino acid supplements. The process caused excellent flocculation and a sizable decrease in chlorine-demand, particularly in the clarified product. Table II illustrates the effect of the process on supplemental amino-nitrogen from glutamic acid. A sterilized pair of samples was included to evaluate the importance of microorganisms in the changes.

It is clearly evident that the sterilized samples were arrested in flocculation and in deamination of glutamic acid. The large increase in ammonia nitrogen in the aerated raw sample illustrates the deamination of glutamic acid in this situation. The progressive loss of Kjeldahl nitrogen, moving from I-D, through II-D, and III-D, represents deamination in the aeration treatment, and sediment nitrogen in the settling step. Both the analyses and the appearance of the samples emphasize the importance of microbial activity in bringing about flocculation.

It is evident from accompanying demand studies, that removal of sediment increases susceptibility to chlorination. This has been established by a series of chlorine residual determinations.

Optimum sedimentation or filtration is theoretically desirable before chlorination also, because many bacteria are removed with the floc. Some of these clumped organisms probably are less susceptible to chlorination than the dispersed cells that escape clarification.

The removal of sediment from sewage aerated with fecal microorganisms is consistently associated with a demand decrease of approximately 25%. This applies to a sewage that has been initially settled about 30 minutes prior to aeration. The difference will be much greater with less sludge removed initially. A bonus factor of optimum aeration is the conditioning of sewage, so that optimum clarification, with its many benefits, can be accomplished.

The Kjeldahl analysis difference between C-II and D-II represents proteinaceous nitrogen remaining from the glutamic acid after aerobic microbial attack. A 6.6* ppm concentration of nitrogenous substances survived the treatment. The low chlorine demand of sample III D makes it seem doubtful that this is still in the amino acid state. This fraction is probably made up of soluble protein and polypeptide fractions formed simultaneously with the formation of the cellular protein removed as precipitate. Chlorine demand studies carried out with this experiment indicated that the 15 ppm of nitrogen added as glutamic acid increased the demand by

*Difference between samples III D and III C.

3.6 ppm of chlorine; the 6.6 ppm of soluble nitrogen remaining from this after aeration was associated with an increase of 0.34 ppm of chlorine demand. This is only 21% of the glutamic acid demand valve.

Phenylalanine is strikingly different from glutamic acid in that no ammonia is released from the former during overnight aeration in raw sewage. Direct comparisons have been made in parallel runs with phenylalanine producing no detectable ammonia, and glutamic acid, yielding about one-third of its nitrogen as ammonia. Prolonged microbial attack undoubtedly will deaminate phenylalanine, but it is strikingly slower than glutamic acid. The demand drop for phenylalanine is considerable during the aeration process, but not quite equal to that observed for glutamic acid. Typical nitrogen changes occurring in aerating sewage with phenylalanine appear in Table III. Sewage aerated with 15 ppm of supplemental phenylalanine-nitrogen dropped in chlorine-demand to 40% of the initial value.

4. Toxic Chlorination Products

Cystine and cysteine have been noted to show atypical amino acid behavior. Both compounds exhibit an extremely high chlorine demand, but do not exhibit the characteristic inhibition of chlorine disinfection. The products of chlorination appear to be bactericidal. This phenomenon has also been noted with uric acid, high in demand, but having little or no interference with chlorine disinfection. The actions of these compounds in a chlorinated sewage demonstrate that toxic compounds may be formed on chlorination.

The most significant aspect of the formation of toxic chlorine compounds during the chlorination of sewage is the potential of the effluent for destroying aquatic life. Many fish and other aquatic organisms are far more sensitive than bacteria to toxic compounds. Chlorination of sewage has been prohibited in England because of associated toxic compounds. This feature of the problem lends great importance to the perfection of a dechlorinating activated sludge system. The effluent of such a system has been demonstrated, in a preliminary test, to be very low in toxicity to minnows. Destruction of labile, toxic chlorine compounds will take place in the activated sludge system, as well as chlorine reduction by the action of nitrites.

The previously named compounds that form toxic chlorination products were found to be destroyed in sewage aerated before chlorination. Projected activities will determine the efficiency of the activated sludge final treatment in destroying toxic compounds.

Figures 1 and 2 illustrate the influence of cysteine and uric acid on the destruction of E. coli by chlorine.

5. Subchlorination - Sometimes Due to Toxic Products, but also a Mixing Phenomenon

Subchlorination may be partially explained on the basis of bactericidal products formed during chlorination. Our studies have not encountered subresidual chlorine levels in domestic sewage that give satisfactory disinfection, nor were any of the reported

subchlorination practices that were reviewed, regarded as satisfactory (2, 3). A stable residual chlorine level of 0.50 ppm or higher, for an adequate contact time, appears to be essential for satisfactory disinfection. The subresidual chlorine disinfection reported in the literature largely deals with the destruction of E. coli to the extent of 40 to 98%. This cannot be regarded as a safe range because many pathogens, i.e., tubercle bacilli and Amoebae cysts, are far more resistant than E. coli.

It must be reemphasized that subchlorination rates have rarely produced effective disinfection; on the other hand, high chlorine residuals are known to produce reliable extent of destruction. There is always some destruction of E. coli by chlorine, even when it is added to sewage with an interfering agent. The chlorine will kill some bacteria as it contacts the sewage and as it disperses and reacts with quenching agents. This effect will be most notable in a high demand sewage requiring a high chlorine dosage. The occasionally encountered subresidual effect is partially explained by initial killing that occurs in disinfectant blending.

6. Activated Sludge Destruction of Chlorine

In sewage chlorination, a relatively stable residual chlorine level of 0.50 ppm or higher is required for efficient disinfection. It has been further demonstrated that biocidal chlorine products, such as those formed with cystine, cysteine, and uric acid, remain in sewage even though little or no residual chlorine is detected.

It was brought out in the previous report that, due to the production of nitrite in an activated sludge system, dechlorination could be achieved. A preliminary demonstration of the process has been carried out (1). It was suggested that such a system could be carried indefinitely, and that chlorine toxicity could be eliminated in the effluent. An activated sludge system as just described has now been carried five months. The product of sludge treatment was compared to influent chlorinated sewage in a fish toxicity test conducted by the Aquatic Biology Division*. The activated sludge effluent 24-, 48-, and 96-hour median tolerance limit was 100%, while the influent chlorinated sewage value was only 10%. The dechlorinated product, diluted ten-fold, had the same toxicity level as undiluted activated sludge effluent. The fish toxicity studies confirmed chemical tests indicating that the chlorine had been destroyed during the activated sludge process.

Survival studies were also carried out using the indicator organisms of the coliform, fecal coliform, and fecal streptococcus groups. Results are given in Table IV and Figure 3. Counts indicated that indicator organisms were present in the activated sludge effluent from the treatment of chlorinated sewage at much less than 1% of the unchlorinated sludge effluent level. Detectable concentrations of viable indicator organisms could not survive the

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*See attached memorandum.

severe chlorination imposed prior to activated sludge treatment. The organisms counted in Table IV and presented in Figure 3 represent natural inhabitants of the sludge system. Some further studies are required for more specific classification.

From these combined studies of chlorinated effluent toxicity and bacteriological survival, it can be concluded that the combined systems of well-managed chlorination and dechlorination will result in a pathogen-free, non-toxic, low-indicator-organism sewage effluent.

7. Temperature Effect

A number of death rate studies were made on E. coli in pasteurized and clarified sewage at 28° and 3°C. The usual retarding effect of low temperature on the killing rate was invariably encountered. Figure 4 and Table V present typical data.

A follow-up observation was made on the 3°C sample. Fresh inoculum was added to the dechlorinated sewage after storing overnight (15 hours). The initial count of 1.4×10^6 per ml fell to 2.2×10^3 in four hours, and to less than 100 per ml in 7 hours. Companion samples, with more chlorine, exhibited higher death rates. Bactericidal action was continuing over an extremely long period in the 3°C samples.

Two important conclusions are illustrated:

(1) Lowering of the temperature of chlorination markedly slows disinfection.

(2) Disinfection continues over a very long period in chilled sewage.

It follows that some adjustments must be made when varying temperatures are encountered in sewage chlorination. More time (or increased chlorine level) must be utilized in cold sewage. A fixed chlorine dosage, however, appears to have the potential ability to kill as many bacteria in cold sewage as in warm sewage. A longer contact time must be allowed for completion of the action at the lower temperature.

Increased chlorine dosage to compensate for the decrease in killing rate at low temperatures threatens disastrous destruction of aquatic life in a haphazard operation. On the other hand, chlorine levels sufficiently high to virtually free the sewage of pathogens in a few hours can be utilized and the chlorine removed by an activated sludge process. It is of the greatest importance that standards be adopted to meet both adequate disinfection requirements and safe toxicity levels for the receiving water.

Indicated processes deliver a pathogen-free effluent harmless to aquatic life.

It appears to be essential to warm cold sewage in order to obtain color development in a reasonable time with the orthotolidine test. Much additional work is essential for establishing acceptable standards for checking chlorine content and establishing treatment time-chlorine content-temperature relationships for sewage.

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3. Feng, T. H. Subchlorination of Wastewater. J. Water Pollution Control Fed., 35:417 (1963).

OPTIONAL FORM NO. 10
1010-104

UNITED STATES GOVERNMENT

Memorandum

TO : Dr. C. E. Rhines

DATE: December 4, 1963

Thru: Dr. Clarence M. Tarzwell
Chief, Aquatic Biology

FROM : Quentin H. Pickering
Fisheries Research Biologist, DWS&PC

SUBJECT: The Acute Toxicity Toward Fathead Minnows of Two Types of Sewage

Exploratory bioassays were conducted on two samples of sewage. The toxicity tests were conducted according to the bioassay method for the evaluation of acute toxicity of industrial wastes and other substances to fish (Standard Methods for the Examination of Water and Waste Water. American Public Health Association, Inc., New York). Because of the small volume of waste, only exploratory tests were conducted. Two small fathead minnows were used in two liters of each test concentration. Concentrations of wastes were prepared in a logarithmic series of numbers, ranging from 100 to 5.6 percent. Dilution water was Newtown Hatchery spring water and had a pH of 7.5. The bioassays were conducted at a temperature of 25° C.

Results

A. Activated sludge - The 24-, 48-, and 96-hour TL_m (median tolerance limit) value was 100 percent. There was no mortality at 56 percent.

B. Chlorinated Sewage - The 24-, 48-, and 96-hour TL_m value was 10 percent. There was no mortality at 5.6 percent. In the higher test concentrations mortality was very rapid. The 100 percent test concentration killed all of the fish in 20 minutes. In 40 minutes all the fish were killed in 56 and 32 percent. The test concentration of 18 percent killed half of the test fish in three hours.

Remarks

The TL_m values given for these two wastes are concentrations that produce 50 percent mortality in the respective time intervals. Chlorine is more toxic to fish under continuous exposure conditions and at low pH. A safe concentration for aquatic life would be considerably lower, possibly one-tenth the TL_m values given, depending on conditions of exposure and the type of aquatic population.

Quentin H. Pickering

TABLE I

DECREASE IN CHLORINE DEMAND DURING AERATION AND SETTLING

Date	Aeration period	Final demand as % of original
10/28/63	overnight	25*
11/1/63	5 hours	38*
	3 days	< 38
11/4/63	5 hours	50*
11/5/63	15 hours	33*
	16 hours	22*
	24 hours	23.5*
	40 hours	25
	7 days**	26
	7 days***	37
11/6/63	17 hours	43*
11/7/63	4 hours	55
	20 hours	8.4*
11/12/63	overnight	28*
11/21/63	20 hours	17*
12/5/63	18 hours	40*

*Average of values - 30.

**Sludge removed after 3 days.

***Sludge not removed until demand determinations.

TABLE II

NITROGEN ANALYSES OF AERATED SEWAGE

Sample	Group*	NH_3-N ppm	Kjeldahl-N ppm
I Starting sample	A	9.5	6.6
	B	9.6	21.9
	C	12.2	6.9
	D	12.8	21.9
II Aerated sample	A	9.2	6.4
	B	8.8	22.0
	C	11.0	7.6
	D	17.9	16.1
III Aerated sample, clarified	A	9.1	6.1
	B	9.2	21.4
	C	11.6	3.7
	D	17.4	10.3

*Key to Group symbols:

A = Autoclaved sample.

B = Autoclaved sample + 15 ppm glutamic acid-nitrogen.

C = Raw sewage control.

D = Raw sewage + 15 ppm of glutamic acid-nitrogen.

TABLE III

NITROGEN CHANGES IN SEWAGE SUPPLEMENTED WITH PHENYLALANINE

Sample	Group*	NH_3-N ppm	Kjeldahl-N ppm
Starting sample	A	11.6	7.3
	B	11.5	9.6
	C	11.5	20.8
Aerated sample	A	10.3	8.0
	B	10.3	11.3
	C	9.3	22.8
Aerated sample, clarified	A	10.1	2.4
	B	10.2	2.8
	C	8.7	12.1

*Key to Group symbols:

A = Raw sewage.

B = Phenylalanine; 3 ppm nitrogen supplement.

C = Phenylalanine; 15 ppm nitrogen supplement.

TABLE IV

MEMBRANE FILTER DETERMINATIONS OF BACTERIAL SURVIVAL IN A DECHLORINATING ACTIVATED SLUDGE SYSTEM

Group*	Sample		
	Raw sewage	Activated sludge effluent	Activated sludge effluent, chlorinated sewage
	Organisms/ml	Organisms/ml	Organisms/ml
A	2.6×10^{4}	4.4×10^{2}	1.0×10^{-1}
B	4.5×10^{3}	2.0×10^{2}	1.5×10^{-1}
C	2.7×10^{3}	1.6×10^{1}	5.0×10^{-2}

*Key to Group symbols:

A - Coliform; M-Endo MF

B - Fecal Coliform; M-FC

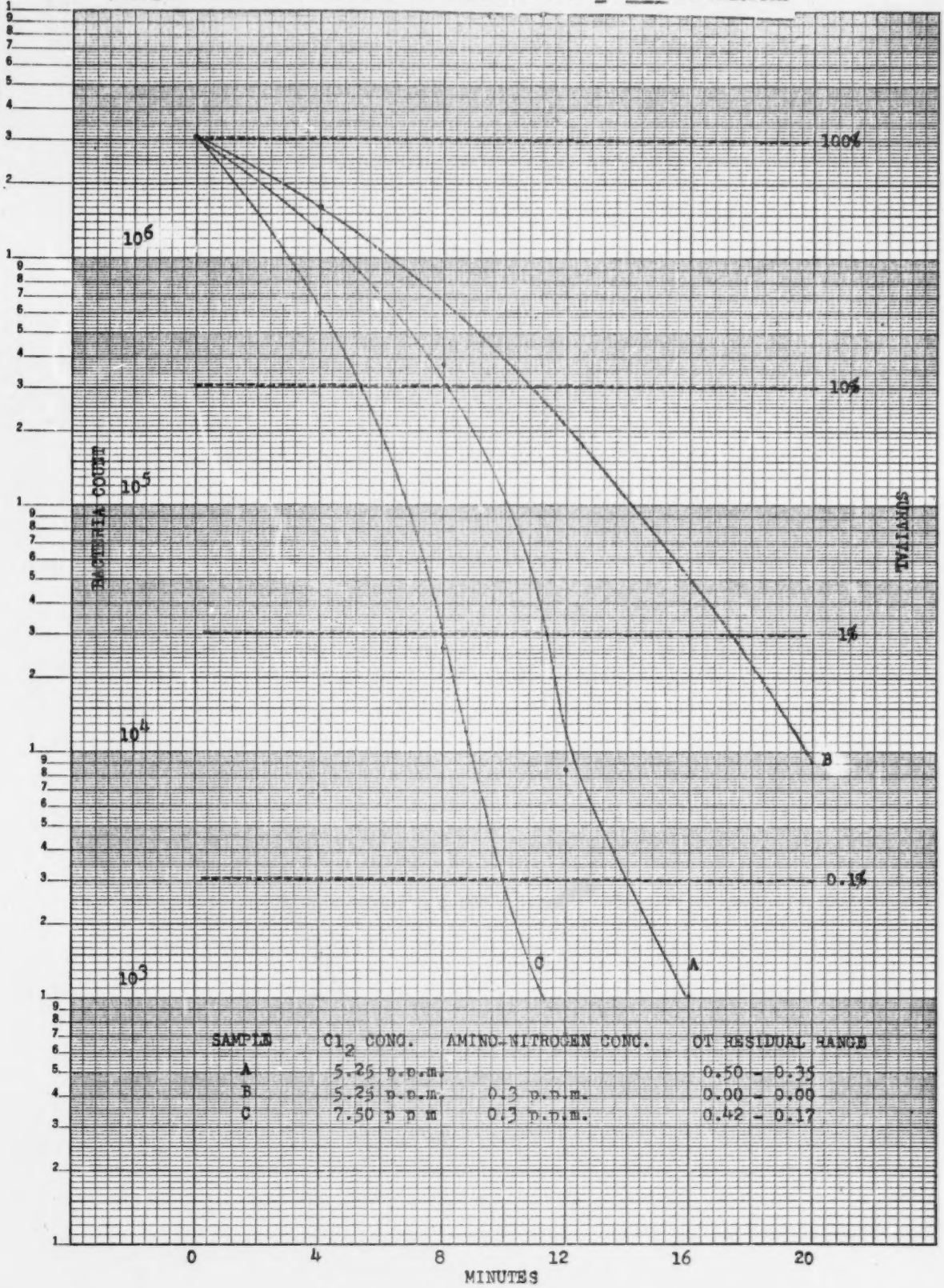
C - Fecal Streptococcus; M-Enterococcus Agar

TABLE V

INFLUENCE OF TEMPERATURE ON SURVIVAL OF E. COLI IN SEWAGE TREATED WITH 4.5 PTM OF CHLORINE

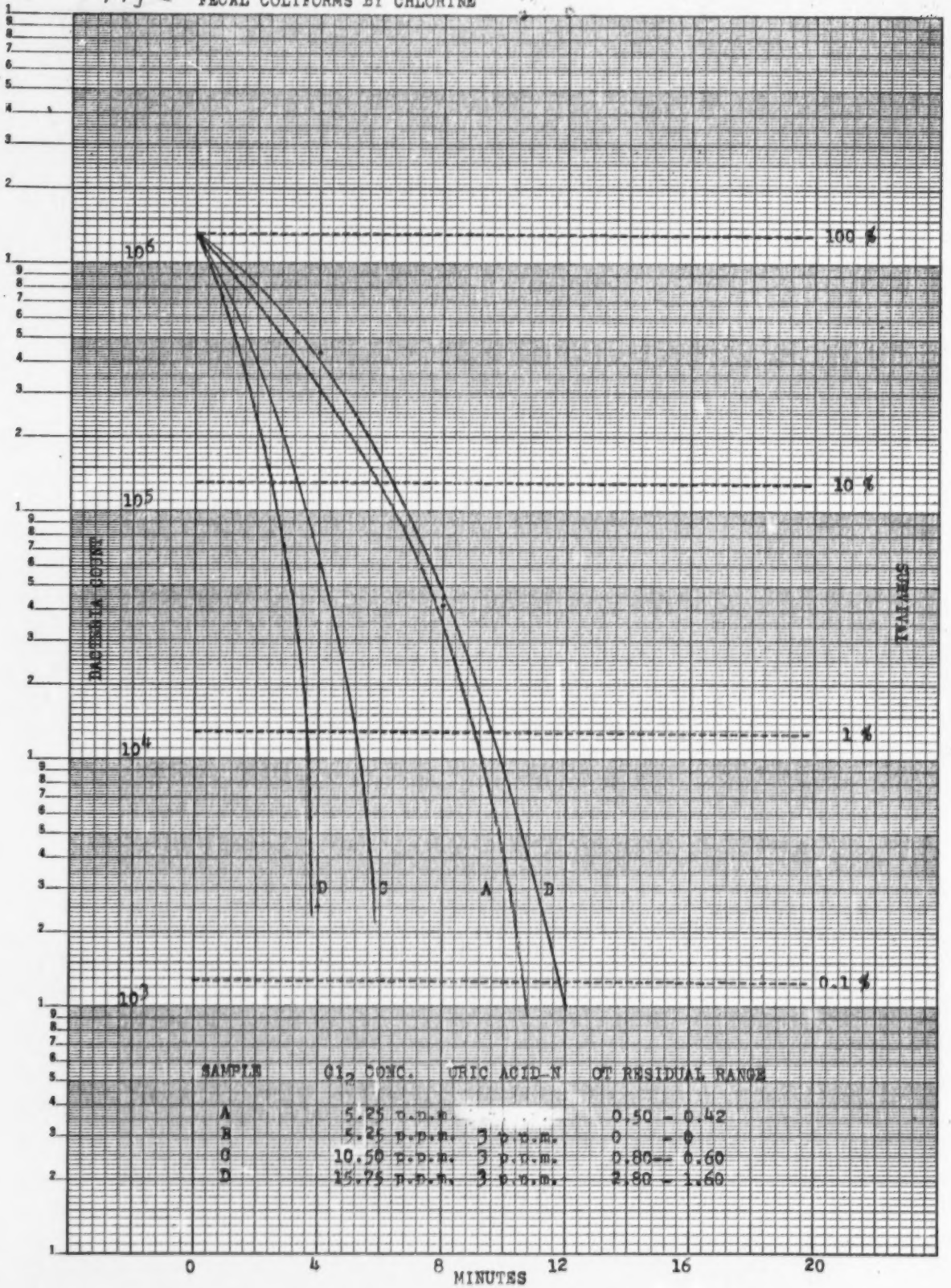
Sample	Temperature °C	Min. chlorination	Organisms/ml
Control		0	1.67×10^6
A	28	4	1.1×10^6
		8	4.1×10^5
		12	4.4×10^4
		16	2.8×10^3
		20	4.0×10^2
B	3	60	2.75×10^5
		90	2.47×10^4
		120	2.6×10^3
		150	2.0×10^2
		180	100

FIG. 1 INFLUENCE OF CYSTEINE ON DESTRUCTION OF E. COLI BY CHLORINE



SAMPLE	Cl_2 CONC.	AMINO-NITROGEN CONC.	OT RESIDUAL RANGE
A	5.25 p.p.m.		0.50 - 0.35
B	5.25 p.p.m.	0.3 p.p.m.	0.00 - 0.00
C	7.50 p p m	0.3 p.p.m.	0.42 - 0.17

Fig 2 INFLUENCE OF URIC ACID-NITROGEN ON THE DESTRUCTION OF FECAL COLIFORMS BY CHLORINE



SAMPLE	Cl_2 CONC.	URIC ACID-N	OT RESIDUAL RANGE
A	5.25 p.p.m.		0.50 - 0.42
B	5.25 p.p.m.	3 p.p.m.	0 - 0
C	10.50 p.p.m.	3 p.p.m.	0.80 - 0.60
D	15.75 p.p.m.	3 p.p.m.	2.80 - 1.60

Figure 3. Bacteriological Survival in a Dechlorinating Activated Sludge System

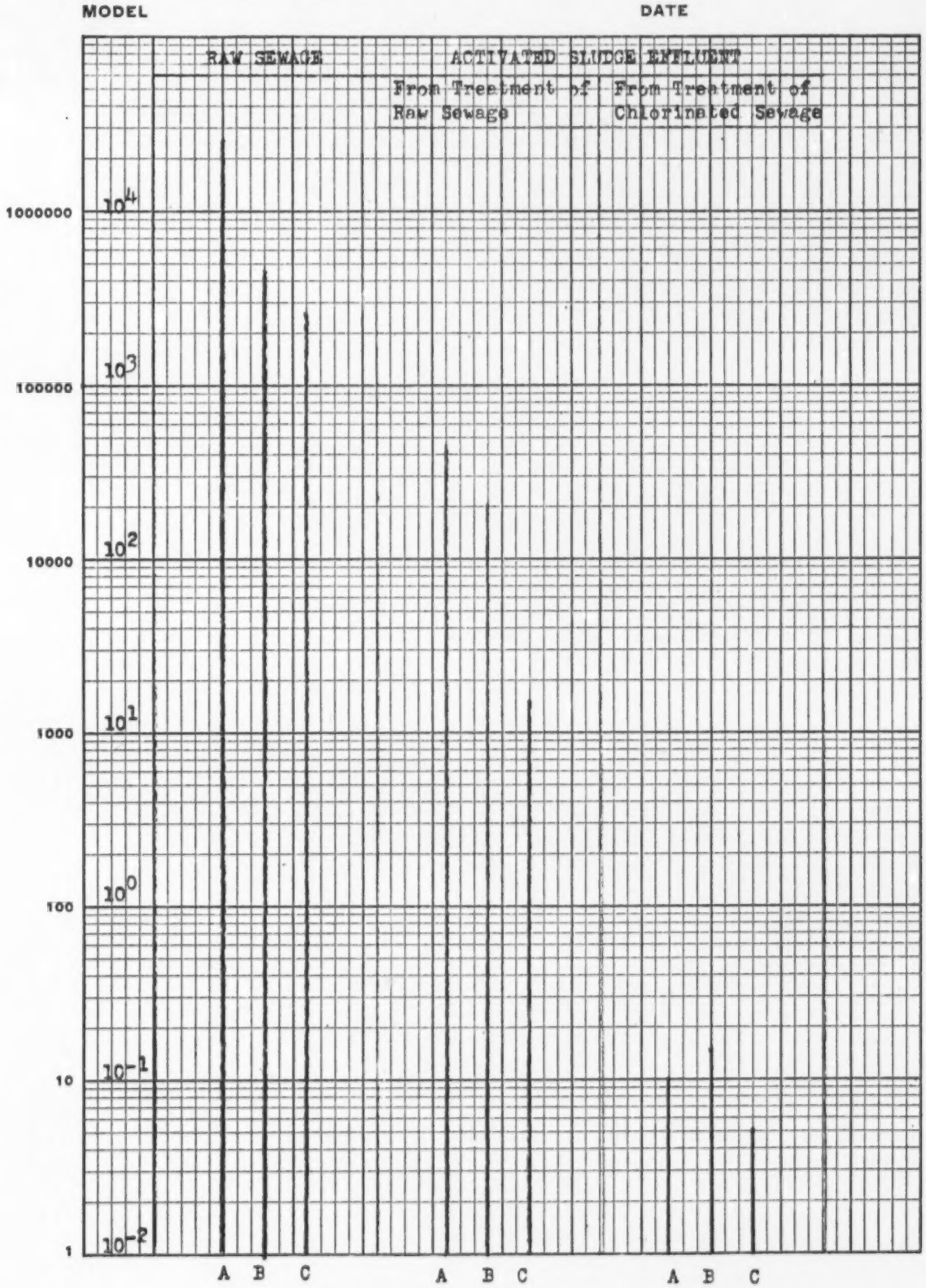


Figure 4. Graphic Presentation of Data of Table V